

# PREFACE

The thesis is devoted to the investigation of complex transition metal oxides exhibiting novel properties such as giant magnetoresistance (GMR), superconductivity and insulator-metal (I-M) transition. Almost all the oxides examined belong to the perovskite family, but contain different transition metal ions. The thesis is divided into three parts.

Part I of the thesis deals with the structure, electron transport properties and magnetoresistance of rare earth manganates of perovskite structure. The various aspects of the manganates investigated are: (i) the defect structure and electron transport properties of  $\text{LaMnO}_3$  with differing  $\text{Mn}^{4+}$  content, (ii) the structure and electron transport properties of  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$  or  $\text{Pb}$ ), (iii) the effect of cation vacancies in the A and B sites on the properties of  $\text{LaMnO}_3$ , study of  $\text{La}_{1-\delta}\text{MnO}_3$  and  $\text{LaMn}_{1-\delta'}\text{O}_3$ , (iv) magnetoresistance and related properties of  $\text{LaMnO}_3$  and  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$  or  $\text{Pb}$ ), (v) the effect of the internal pressure due to the A site cations on the magnetoresistance and related properties of  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{Ln} = \text{La}, \text{Nd}$ , or  $\text{Gd}$ ,  $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$  or  $\text{Pb}$ ), (vi) the effect of particle size on the magnetoresistance and related properties of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ , and (vii) the effect of dimensionality on the magnetoresistance and related properties of the manganates. A study of  $(\text{La}, \text{Sr})_{n+1}\text{Mn}_n\text{O}_{3n+1}$  or  $(\text{SrO}) (\text{La}_{1-x}\text{Sr}_x\text{MnO}_3)_n$ . Studies of these manganates have involved structural characterization as well as magnetic and electrical measurements to examine the I-M transition, GMR and related properties.

Part II of the thesis deals with cuprate superconductors. This section describes (i) the synthesis and characterization of Pb-based cuprate superconductors obtained by the sol-gel method, (ii) the synthesis and characterization of cuprate superconductors prepared by the combustion route, (iii) the synthesis and characterization of simple double layer cuprates of the formulae  $\text{LaSrLnCu}_2\text{O}_8$  ( $\text{Ln} = \text{Y}$  or rare earth)

and  $\text{La}_{2-x}\text{Ba}_x\text{ACu}_2\text{O}_8$  ( $A = \text{Ca}$  or  $\text{Sr}$ ), (iv) the structure and properties of oxyanion derivatives of 123 cuprate superconductors Effects of substitution of carbonate and nitrate ions in the Cu(1) position of  $\text{YBaSrCu}_3\text{O}_{7-\delta}$  and the superconducting borate derivatives of 123 cuprates

Part III of the thesis discusses the electrochemical synthesis of unusual oxides of nickel and manganese The electrochemical method enables the preparation of the transition metal oxides where the transition metals are in higher oxidation states The technique has been employed to prepare  $\text{LaMnO}_3$  compositions with high  $\text{Mn}^{4+}$  content exhibiting ferromagnetism and I M transition Similarly, stoichiometric  $\text{NdNiO}_3$  has been prepared electrochemically This material so prepared is metallic unlike the  $\text{NdNiO}_{3-\delta}$  samples of which are reported in the literature as exhibiting M-I transition Lastly, the unusual metal oxides of the composition  $\text{Ln}_3\text{Ni}_4\text{O}_{17}$  ( $\text{Ln} = \text{La}, \text{Pr}$ ) prepared electrochemically have been investigated

The work presented in this thesis was carried out by the candidate as a part of the Ph D training programme He hopes that the present investigations will provide a worthwhile contribution to the existing understanding of the three major phenomena in solid state chemistry such as giant magnetoresistance, superconductivity and metal-insulator transition